



**You have downloaded a document from
RE-BUŚ
repository of the University of Silesia in Katowice**

Title: Application of Mossbauer spectroscopy, multidimensional discriminant analysis, and Mahalanobis distance for classification of equilibrated ordinary chondrites

Author: Marek Woźniak, Jolanta Gałązka-Friedman, Duda, Martyna Jakubowska, Patrycja Rzepecka, Łukasz Karwowski

Citation style: Woźniak Marek, Gałązka-Friedman Jolanta, Duda Przemysław, Jakubowska Martyna, Rzepecka Patrycja, Karwowski Łukasz. (2019). Application of Mossbauer spectroscopy, multidimensional discriminant analysis, and Mahalanobis distance for classification of equilibrated ordinary chondrites. "Meteoritics & Planetary Science" (Vol. 54, iss. 8 (2019), s. 1828-1839), doi 10.1111/maps.13314



Uznanie autorstwa - Użycie niekomercyjne - Licencja ta pozwala na kopiowanie, zmienianie, remiksowanie, rozprowadzanie, przedstawienie i wykonywanie utworu jedynie w celach niekomercyjnych. Warunek ten nie obejmuje jednak utworów zależnych (mogą zostać objęte inną licencją).



UNIwersYTET ŚLĄSKI
W KATOWICACH



Biblioteka
Uniwersytetu Śląskiego



Ministerstwo Nauki
i Szkolnictwa Wyższego

Application of Mössbauer spectroscopy, multidimensional discriminant analysis, and Mahalanobis distance for classification of equilibrated ordinary chondrites

Marek WOŹNIAK¹, Jolanta GAŁĄZKA-FRIEDMAN^{2*}, Przemysław DUDA²,
Martyna JAKUBOWSKA², Patrycja RZEPECKA², and Łukasz KARWOWSKI³

¹Faculty of Biology, University of Warsaw, Miecznikowa 1, 02-096 Warsaw, Poland

²Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

³Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland

*Corresponding author. E-mail: jgfrie@if.pw.edu.pl

(Received 25 January 2018; revision accepted 16 May 2019)

Abstract—Mössbauer spectra of equilibrated ordinary chondrites consist of two doublets due to paramagnetic iron present in olivines and pyroxenes and two sextets due to magnetically ordered iron present in metallic phases and troilite. The spectral areas of the different mineralogical phases found by Mössbauer spectroscopy in meteorites are proportional to the number of iron atoms in this mineralogical phase. This property of Mössbauer spectra can be the basis for constructing a method for the classification of ordinary chondrites. This idea was first explored at the Mössbauer Laboratory in Kanpur. This group suggested a qualitative method based on 2-dimensional plots of Mössbauer spectral areas and thus classified properly some meteorites. We constructed a quantitative method using Mössbauer spectral areas, multidimensional discriminant analysis, and Mahalanobis distance (4M method) to determine the probability of a meteorite to be of type H, L, or LL. Based on 59 Mössbauer spectra, we calculated by the 4M method, S_{cluster} , the *level of similarity* of the Goronyo meteorite to the clusters. On the plot of ferrosilite versus fayalite, the point representing Goronyo is located on the border between H and L areas. Calculated by the 4M method, the meteorite Goronyo is 32% similar to type H, 75% to type L, and 11% to type LL. Additional mineralogical analyses suggested that the Goronyo meteorite would be classified as type L, although it was originally reported as type H in the Meteoritical Bulletin Database.

INTRODUCTION

Mössbauer spectroscopy, based on the Mössbauer effect (discovered in 1958), has a very high-energy resolution (typical value 10^{-12}). This technique is applicable to different isotopes, but the most widely used is ^{57}Fe . In meteoritics, Mössbauer spectroscopy was applied for identifying different mineral phases and for studying weathering processes (Bland et al. 1998). Since 2000, Mössbauer spectroscopy has been applied for the classification of ordinary chondrites (Paliwal

et al. 2000). The basis for these studies was an observation of some systematics of Mössbauer spectral areas of Fe-containing minerals in ordinary chondrites.

The area of a Mössbauer spectrum is dictated by n (the number of ^{57}Fe nuclei in a compound) and the Mössbauer efficiency (the f -factor) for this compound. Assuming roughly equal f -factors for different iron-containing minerals present in a meteorite, the relative areas of the Mössbauer spectrum obtained for each mineral is proportional to the relative amount of this mineral in the studied chondrite. This feature can be the basis for constructing a method for classifying ordinary chondrites.

Paliwal et al. (2000) performed systematic studies of the possibility of applying Mössbauer spectroscopy to the classification of ordinary chondrites, by measuring the percentages of spectral areas from different mineral

[Correction added on 1st July 2019, after first online publication: in first sentence of the abstract, strange letter A appeared inside the sentence “Mössbauer spectra of equilibrated ordinary chondrites A consist of two doublets...” which was removed]

phases in the Mössbauer spectra. They applied Mössbauer spectroscopy for reclassifying an undocumented meteorite which fell on August 12, 1991 in India. This meteorite was classified as an enstatite chondrite, but these authors showed it to be a H5 chondrite.

The same group (Verma et al. 2002) applied various types of plots (e.g., area in Mössbauer spectra of metallic phase versus nonmetallic phase, area of metallic phase versus area for silicate phase, and area of pyroxene versus area of olivine) to define different regions typical for ordinary chondrites types H, L, and LL. Later Verma's group (Verma et al. 2003) constructed a baseline of 24 ordinary chondrites and observed the systematic behavior of spectral areas from all main mineralogical phases present in these 24 ordinary chondrites of types H, L, and LL.

The idea of Verma was subsequently explored by groups from Ekaterinburg (Oshtrakh et al. 2008; Maksimova et al. 2018) and from Canberra (Elewa and Cadogan 2017). The latter group worked on the database of Verma, which was used to construct 2-D plots. On these plots, they delimited three different regions (for types H, L, and LL). The aim of their study was to determine the chemical group of the Lynch-001 ordinary meteorite. According to the official classification, Lynch-001 is a brecciated L5/6 ordinary chondrite with minor to medium weathering.

In the paper by the Ekaterinburg group from 2008 (Oshtrakh et al. 2008), the Mössbauer spectra of 11 ordinary chondrites types H and L were measured at room temperature with high-velocity resolution, using 4096 channels. On seven 2-D plots, prepared for various variables, e.g., area of pyroxene versus area of olivine, area of metal or (metal + iron oxide) versus area of (olivine + pyroxene), arbitrary straight lines were included to distinguish various ordinary chondrites of type H from type L. Another Mössbauer paper from 2018 (Maksimova et al. 2018) showed only one plot related to the classification of meteorites. Meteorites NWA6286 and NWA7857 were in the region belonging to ordinary chondrites type LL.

Our group has published three papers on this subject (Gałązka-Friedman et al. 2014, 2017; Szlachta et al. 2014). During the analysis of the data collected (Gałązka-Friedman et al. 2017), we reached the conclusion that the most effective way of applying Mössbauer spectroscopy to the classification of meteorites should be based on simultaneous application of comparative analysis of four values of spectral areas found in the spectra of ordinary chondrites associated with olivine, pyroxene, metallic phases, and troilite. For this purpose, we applied multidimensional discriminant analysis (MDA) introduced to statistics by R. Fischer in the 1930s (Fisher 1936). This is a very effective method for

classifying an object, when the group it belongs to is unknown.

When applying the MDA method, we also used the Mahalanobis distance, which is the distance between two points in an n -dimensional space (Mahalanobis 1936). It grades the contribution of individual components and employs the correlations between them. It can be used for determining the similarity between an unknown random vector and a vector from a known set.

In the next section, as an example, the Mössbauer spectra of one ordinary chondrite of type H (Carancas), one of type L (New Concord), and one of type LL (NWA7733) are shown and discussed. Their spectral areas will be compared with the mean values of the spectral areas of the meteorites present in our database, which is built on Mössbauer data from 41 meteoritic samples of ordinary chondrites prepared and measured in Warsaw, and 18 Mössbauer data taken from the literature. Such a comparison will be performed also for Goronyo (H4). Justification for including Mössbauer spectra areas measured in different laboratories into one database had been presented by Bogusz et al. (2018).

We describe our 4M method, and using this method, we attempt to find to which type of ordinary chondrites the meteorite Goronyo is the most similar. We decided to use meteorite Goronyo for testing the 4M method because on the plot ferrosilite (Fs) versus fayalite (Fa) the meteorite Goronyo is between the region occupied by type H and type L. Our preliminary Mössbauer studies suggested that meteorite Goronyo is rather similar to type L, although it was reported as type H in the Meteoritical Bulletin (Connolly et al. 2006).

MÖSSBAUER SPECTROSCOPY—MATERIAL AND EXPERIMENTAL RESULTS

Samples of bulk meteorites were crushed and ground into fine powder in an agate mortar under ethyl alcohol. Then, the powdered samples were loaded into special absorber holders (diameter 1.4 cm). The weights of the samples were within the range from 70 to 120 mg.

Mössbauer spectra were measured at room temperature with a conventional Mössbauer spectrometer. The meteorite samples were measured at different times, so the activity of the ^{57}Co in-Rhodium source was not the same in all measurements (between 15 and 100 mCi). The 14.4 keV gamma rays were detected by a proportional counter. A few million (from one to six) counts/channel for every sample were collected in 512 channels and then folded to 256 channels. The meteorite Goronyo was measured with 17 million counts/channel. The velocity scale was calibrated using an α -iron metal foil

absorber at room temperature. The spectra were fitted using the Recoil program (Lagarec and Rancourt 1998). All experimental Mössbauer spectra were fitted with Lorentzian lines. The ratio of intensity of the lines in a sextet was fixed as 3:2:1. To obtain correct Mössbauer parameters for troilite, the fitting procedure “Full Static Hamiltonian” was applied (Hafner et al. 1967). As the troilite has an axial symmetry, only the angle theta (the angle between the direction of the magnetic field and the main axis of the electric field gradient) was fitted. Mössbauer data with spectral area of ferric iron higher than 7% were not included for further analysis.

The percentage of the spectral areas of olivine, pyroxene, metallic phases, and troilite in Mössbauer spectra were measured in the following nine H chondrites: Pułtusk, Grzempach, Kidairat, Carancas, Juancheng, Tamdakht, Bassikounou, Buzzard Coulee, and Zag. More values were taken from the literature for 13 meteorites: Noblesville, Xingyang, Wuan (Verma et al. 2002); Allegan, Didwana, Gujargaon (Verma et al. 2003); Košice (Lipka et al. 2013); Ochansk, Richardton, Vengerovo, Zvonkov (Oshtakh et al. 2008); Torino (Ortalli and Pedrazzi 1990); and Xingyang (Zhang et al. 1994).

The percentage of the spectral areas of the above-mentioned different mineral phases were also obtained for 18 L chondrites: Barwell, Colby (Wisconsin), Farmington, Mount Tazerzait, Ohuma, Softmany, Elenovka, Katol, Battle Mountain, Mreïra, Saratov, Beni M'hira, Xining, New Concord, Katagum, Hyattville, and two different samples of meteorite Shisr 176 (a and b). Similar values were taken from the literature for two meteorites: Kunashak (Oshtakh et al. 2008) and New Halfa (Abdu and Ericsson 1997).

The percentage of the spectral areas of the different mineral phases were further obtained for 14 samples of ordinary chondrites type LL: Kilabo, NWA4841, NWA7313, NWA8590, NWA8602, Benguerir, Oued el Hadjar, Mahbas Arraid, NWA7314, NWA7733, NWA4883, NWA6287, and two different samples of Chelyabinsk (a and b). Similar values were taken from the literature for meteorites: Bandong, Bhawad, and Tuxtuac (Verma et al. 2003). The results for all these meteorites were used as our database. We also measured the meteorite Goronyo.

In Figs. 1A–C, Mössbauer spectra of ordinary chondrites of different types (Carancas—type H, New Concord—L, and NWA7733—LL) are shown as examples. In Fig. 1D, the Mössbauer spectrum of the meteorite Goronyo is presented. The Mössbauer parameters of all these four meteorites are given in Table 1.

As seen in Table 1, the Mössbauer parameters (IS, B, and QS) obtained for olivine, pyroxene, and the

metallic phases are similar in the different meteorites. For troilite, the quadrupole interaction parameters (QS) differ somewhat. This may be due to different amounts of vacancies or impurities in different troilites (Ok et al. 1982; Baek et al. 1984; Kruse 1990). In contrast, the cause of different Mössbauer parameters for ferric iron is due to different products of the weathering process (Bland et al. 1998). Percentages of spectral areas for all investigated ordinary chondrites types H, L, and LL are shown in Table S1 in supporting information.

The most characteristic feature in the Mössbauer spectrum of Carancas (Fig. 1A) is a significant subspectrum due to the metallic phases (26.6%), which is higher than the mean value found in our database for ordinary chondrites type H (17.3%). The metallic phases were fitted by two subspectra: kamacite (spectral area = 18.1%) and taenite (spectral area = 8.5%). Ferric iron (a result of terrestrial weathering) is represented by a doublet with a spectral area of 3.6%. The spectral area from olivine (34.6%) is somewhat smaller than the mean value for ordinary chondrites type H in our database (39.2%). The spectral areas of pyroxene (21.9%) and troilite (13.2%) are quite close, respectively, to the mean values of (24.3%) and (16.5%).

The percentages of the spectral areas of all mineral phases in the sample of meteorite New Concord (Fig. 1B) are very close to the mean values of mineral phases of ordinary chondrites type L present in our base: for olivine 49.4% versus 51.3%; for pyroxene 21.7% versus 22.0%; for troilite 16.3% versus 15.7%; and for metallic phases 9.9% versus 8.4%. The spectral area of ferric iron—2.7% is typical for short terrestrial weathering.

The most characteristic feature of the Mössbauer spectrum of meteorite NWA7733 (Fig. 1C) is the very small percentage of kamacite (less than 0.2%) and ferric iron (less than 0.3%). Also, the percentage of troilite is smaller than the mean value in all 17 samples of ordinary chondrites type LL registered in our database (6.7% versus 10.6%). The spectral areas from olivine and pyroxene are higher than the mean values: for olivine 65.8% versus 61.7% and for pyroxene 27.0% versus 24.2%.

Based on Mössbauer spectra of the 59 ordinary chondrites, we tried to find a method for the classification of equilibrated ordinary chondrites. Our database contains Mössbauer data for three clusters—ordinary chondrites types H, L, and LL. These Mössbauer data show the percentage of the spectral areas of the main mineralogical phases present in our meteorites: olivine (ol), pyroxene (pyr), metallic phases (met), and troilite (tr). Based on these data, different 2-D-type plots were constructed. In Fig. 2, examples of such plots are shown.

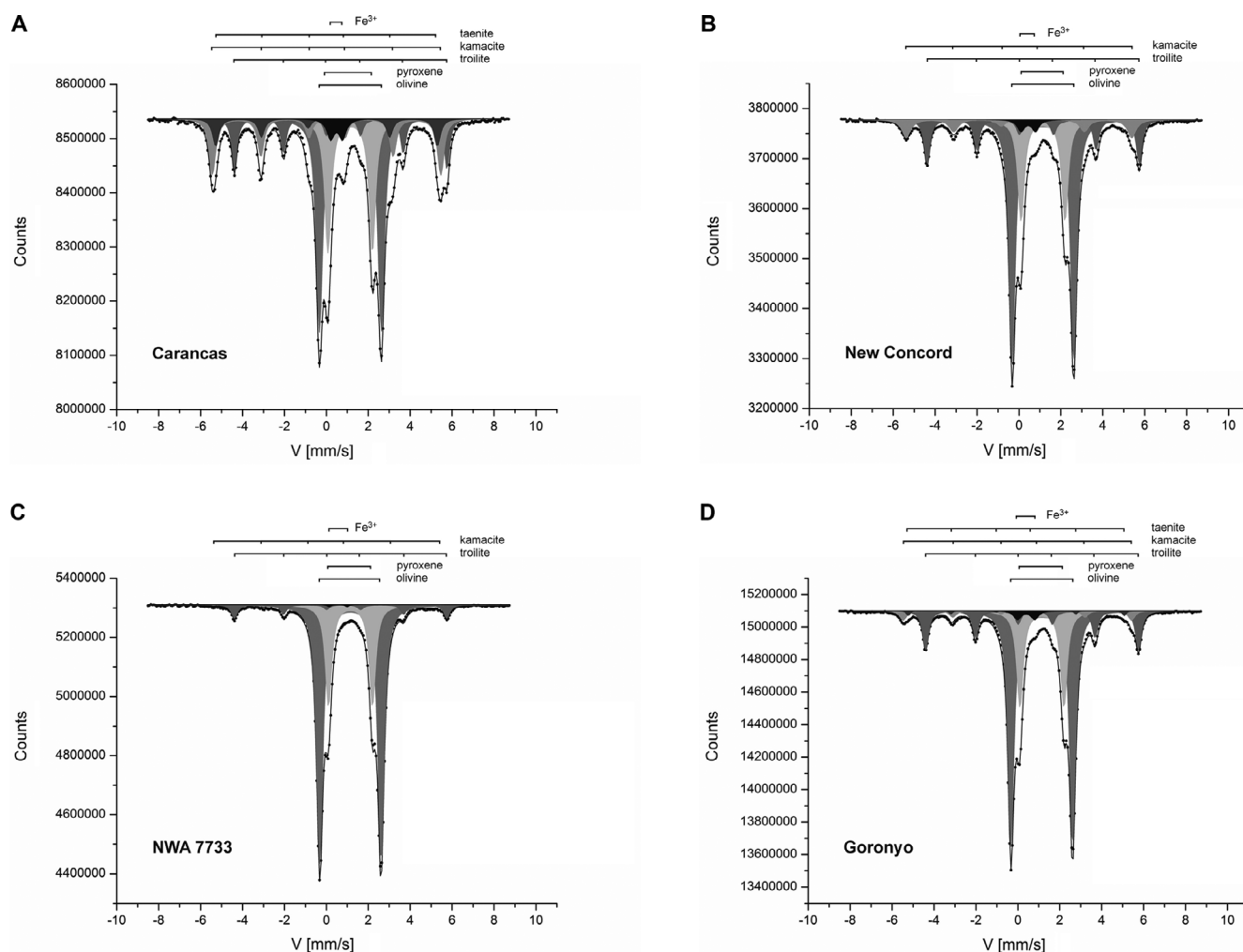


Fig. 1. Mössbauer spectra of ordinary chondrites. A) Meteorite Carancas (type H). B) Meteorite New Concord (type L). C) Meteorite NWA7733 (type LL). D) Meteorite Goronyo (type H).

In Figs. 2 and 3, we can observe the difference between various types of meteorites and can assert that Mössbauer areas could be used for the classification (or verification) of equilibrated ordinary chondrites. One can see that the ranges of correlation between the different mineral phases in the meteorite, as observed by Mössbauer spectroscopy, are distinct, but not completely separate. It may, however, be that the 2-D plots do not show the whole power of discrimination between the four parameters: ol, pyr, met, and tr.

The most characteristic feature of the Mössbauer spectrum of Goronyo (Fig. 1D) is the quite small percentage of spectral area associated with metallic phases (6.1%) compared to the mean value obtained for ordinary chondrites type H (17.3%). There is also a large difference in the percentage of the spectral areas associated with olivine: 52.1% versus 39.2% obtained

for ordinary chondrites type H. These discrepancies have motivated us to test the hypothesis whether the meteorite Goronyo is indeed type H. In the next section, the evaluation of the content of Fa and Fs in Goronyo, with the use of microprobe analysis is described.

MICROPROBE ANALYSIS—METHOD AND RESULTS

Microprobe analyses of selected minerals in the meteorite were carried out in the Inter-Institutional Laboratory of Microanalyses of Minerals and Synthetic Substances, Warsaw, using a CAMECA SX-100 electron microprobe. Analytical conditions were 10 s counting time, 15 kV accelerating voltage, and 20 nA beam current. Standards, analytical lines, diffracting crystals, and mean detection limits (in wt%) were as follows:

Table 1. Mössbauer parameters obtained from the best fit to the experimental spectra of meteorites Carancas, New Concord, NWA7733, and Goronyo.

Ordinary chondrite	Mineral phase	IS (mm s ⁻¹)	B (T)	QS (mm s ⁻¹)	Θ (°)	w (mm s ⁻¹)	A (%)
Carancas type H	Olivine	1.15	—	2.96	—	0.19	34.6
	Pyroxene	1.13	—	2.12	—	0.19	21.9
	Kamacite	0.02	33.8	-0.02	—	0.18	18.1
	Taenite	-0.01	32.8	0.05	—	0.18	8.5
	Troilite	0.75	30.9	0.95	60.8	0.15	13.2
New Concord type L	Fe ³⁺	0.49	—	0.80	—	0.21	3.6
	Olivine	1.15	—	2.94	—	0.18	49.4
	Pyroxene	1.15	—	2.09	—	0.19	21.7
	Kamacite	0.00	33.4	0.00	—	0.24	9.9
	Troilite	0.76	30.9	1.00	61.9	0.16	16.3
NWA7733 type LL	Fe ³⁺	0.44	—	0.60	—	0.20	2.7
	Olivine	1.15	—	2.93	—	0.18	65.8
	Pyroxene	1.15	—	2.10	—	0.19	27.0
	Kamacite	0.01	33.5	0.01	—	0.20	0.2
	Troilite	0.76	31.0	0.90	61.5	0.17	6.7
Goronyo type H (or L?)	Fe ³⁺	0.56	—	0.86	—	0.11	0.3
	Olivine	1.14	—	2.95	—	0.17	52.1
	Pyroxene	1.14	—	2.10	—	0.19	23.0
	Kamacite	0.02	33.8	-0.08	—	0.20	4.7
	Taenite	-0.14	32.0	0.14	—	0.11	1.4
	Troilite	0.76	30.9	1.03	61.6	0.16	16.5
	Fe ³⁺	0.39	—	0.82	—	0.21	2.3

Note: IS = isomer shift; B = internal magnetic field; QS = quadrupole interaction parameter, Θ = angle between direction of the magnetic field and the main axis of the electric field gradient; w = HWHM (half width at half maximum); A = % of spectral area. Experimental uncertainties for cited parameters are the following: for IS—0.01 mm s⁻¹; for QS—0.02 mm s⁻¹; for B—0.2 T; for w—0.01 mm s⁻¹; for A (% of spectral area): for doublet—1.0% and for sextets—2.0%.

rutile—Ti (Kα, PET, 0.03), diopside—Mg (Kα, TAP, 0.02), Si—(Kα, TAP, 0.02), Ca—(Kα, PET, 0.03), K (Kα, PET, 0.03), albite—Na (Kα, TAP, 0.01), hematite—Fe (Kα, LIF, 0.09), rodonite—Mn (Kα, LIF, 0.03), phlogophite—F (Kα, TAP, 0.04), apatite—P (Kα, PET, 0.02), rhodonite—Mn (Kα, LIF, 0.02), hematite—Fe (Kα, LIF, 0.09), CoO—Co (Kα, LIF, 0.04), NiO—Ni (Kα, LIF, 0.03), diopside—Si (Kα, TAP, 0.02), orthoclase—Al (Kα, TAP, 0.02), and ilmenite—Ti (Kα, TAP, 0.03).

In the studied meteorite, two types of pyroxene were observed: hypersthene and a diopside-like phase. The Fs content in the first phase is in the range starting from 19.47% up to 20.26%. The diopside is a rare phase and contains 44.63–45.06% of Wo. Olivine is mainly represented by Fa (22.90–24.31%). Plagioclase forms chondrules as well as the matrix. In the chondrules, maskelynite is noted. Plagioclases are represented by unzoned crystals with the composition as follows: An_{8.84–10.48}, Ab_{84.55–86.89}, and Or_{3.40–6.59}. The maskelynite is slightly rich in K.

Small metallic phases are mainly represented by taenite, rather than by kamacite. The Ni and Co

content in taenite is in the range (wt%) from 32.00 to 39.00 and from 0.16 to 0.22, respectively. The highest concentration of Ni in the studied taenite is in the most marginal parts of the crystals. The Ni and Co content in kamacite is up to 6.40 wt% and 0.75 wt%, respectively.

Other minerals which are typical for ordinary chondrites are represented by troilite (as a small veins with trace of Ni), chromite, and rare phosphates. The phosphates are merrillite and chlorapatite with low fluorine content.

The results of 12 measurements of the content of fayalite are the following: 24.31, 22.90, 24.00, 23.56, 24.55, 23.15, 23.42, 23.19, 23.16, 23.42, 23.63, and 23.44. The mean value and its error are 23.51±0.16.

The results of 12 measurements of the content of ferrosilite are the following: 19.89, 19.47, 19.85, 19.58, 19.89, 20.13, 20.17, 19.68, 20.22, 19.72, and 20.04. The mean value and its error are 19.91±0.08.

Based on these results, the sample of the Goronyo meteorite we analyzed appears to be an L chondrite.

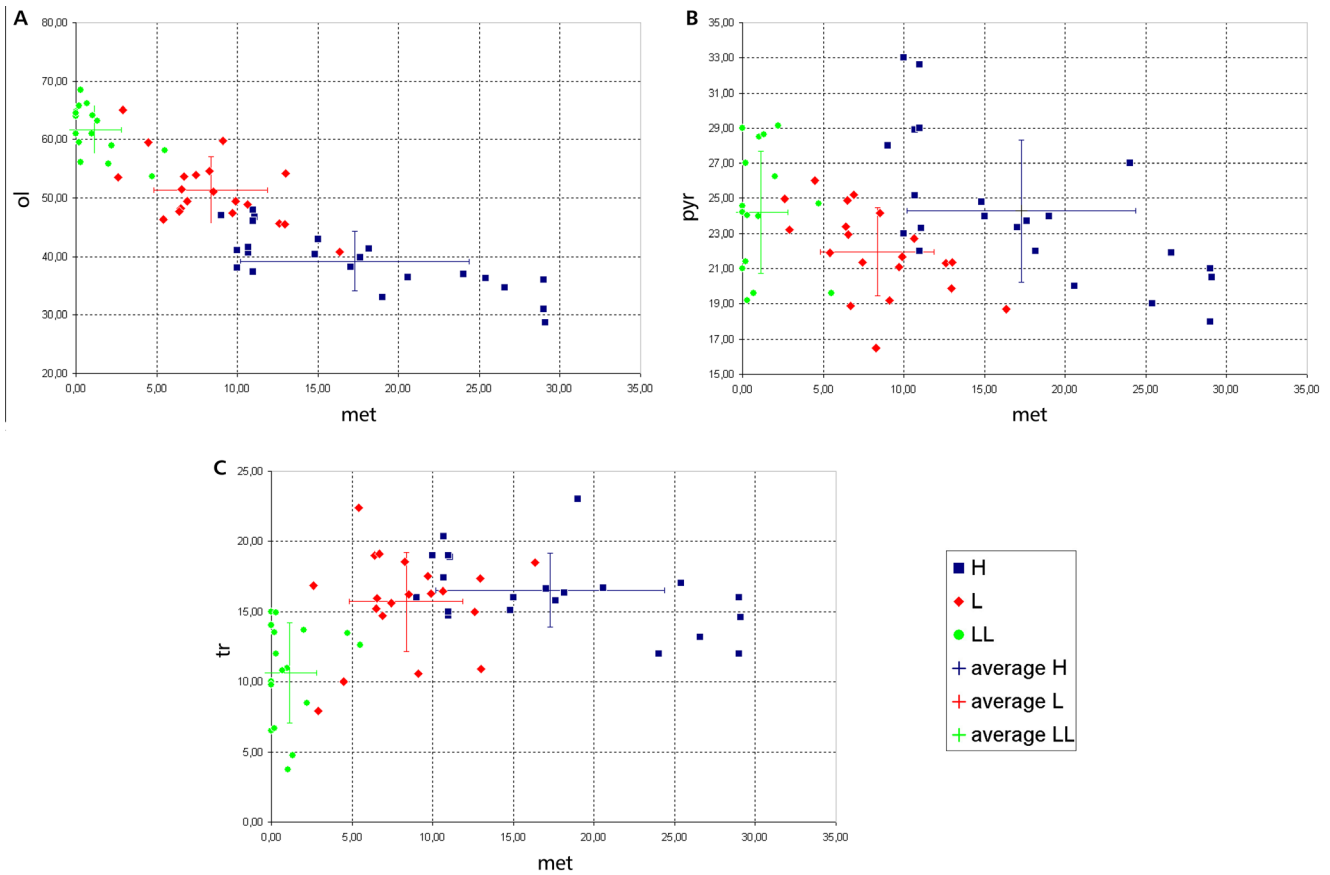


Fig. 2. Percentage of iron obtained by Mössbauer spectroscopy for 59 ordinary chondrites types H, L, and LL. A) Spectral areas from olivine (ol) versus spectral areas from metallic phases (met). B) Spectral areas from pyroxene (pyr) versus spectral areas from metallic phases (met). C) Spectral areas from troilite (tr) versus spectral areas from metallic phase (met).

MULTIDIMENSIONAL DISCRIMINANT ANALYSIS AND MAHALANOBIS DISTANCE—4M METHOD (METEORITES-MÖSSBAUER-MULTIDIMENSIONAL-MAHALANOBIS)

The aim of our study was to check if the percentages of spectral areas determined by Mössbauer spectroscopy have discriminant properties which are analogous to the amount of Fa and Fs used in mineralogical classifications (Mason 1962; Fredriksson and Keil 1964). Will we be able to determine the type of an equilibrated ordinary chondrite using only Mössbauer data?

By analyzing the data obtained by Mössbauer spectroscopy (see Table 2), we tried to determine the type of an equilibrated ordinary chondrite by applying discriminant analysis (Morrison 1990; Krzanowski 2000). Our model consisted of three clusters (three types of equilibrated ordinary chondrites: H, L, and LL). In each of the clusters, there is a set of four parameters (4-dimensional variable $x = [\text{ol}, \text{pyr}, \text{met}, \text{tr}]$).

All values of these four parameters had the same unit (%), but their ranges differ. It is clearly seen (Figs. 2 and 3B) that these parameters (ol, pyr, met, and tr) are correlated. The values of correlations and covariances (presented in Tables 3 and 4) confirm this statement.

On the basis of the 4-D space of parameters, we wanted to determine in an objective way, how far from well-determined clusters (equilibrated ordinary chondrites types H, L, and LL) each investigated meteorite is located.

Due to the existing correlations between Mössbauer spectral data, the Euclidean distance is not a proper method for determining the distance between the point representing our unclassified meteorite and clusters in our model. The correct method is Mahalanobis distance which determines the distance between two points in n -dimensional space with compliance of the contribution of different variances and existing correlations between them (see Appendix A).

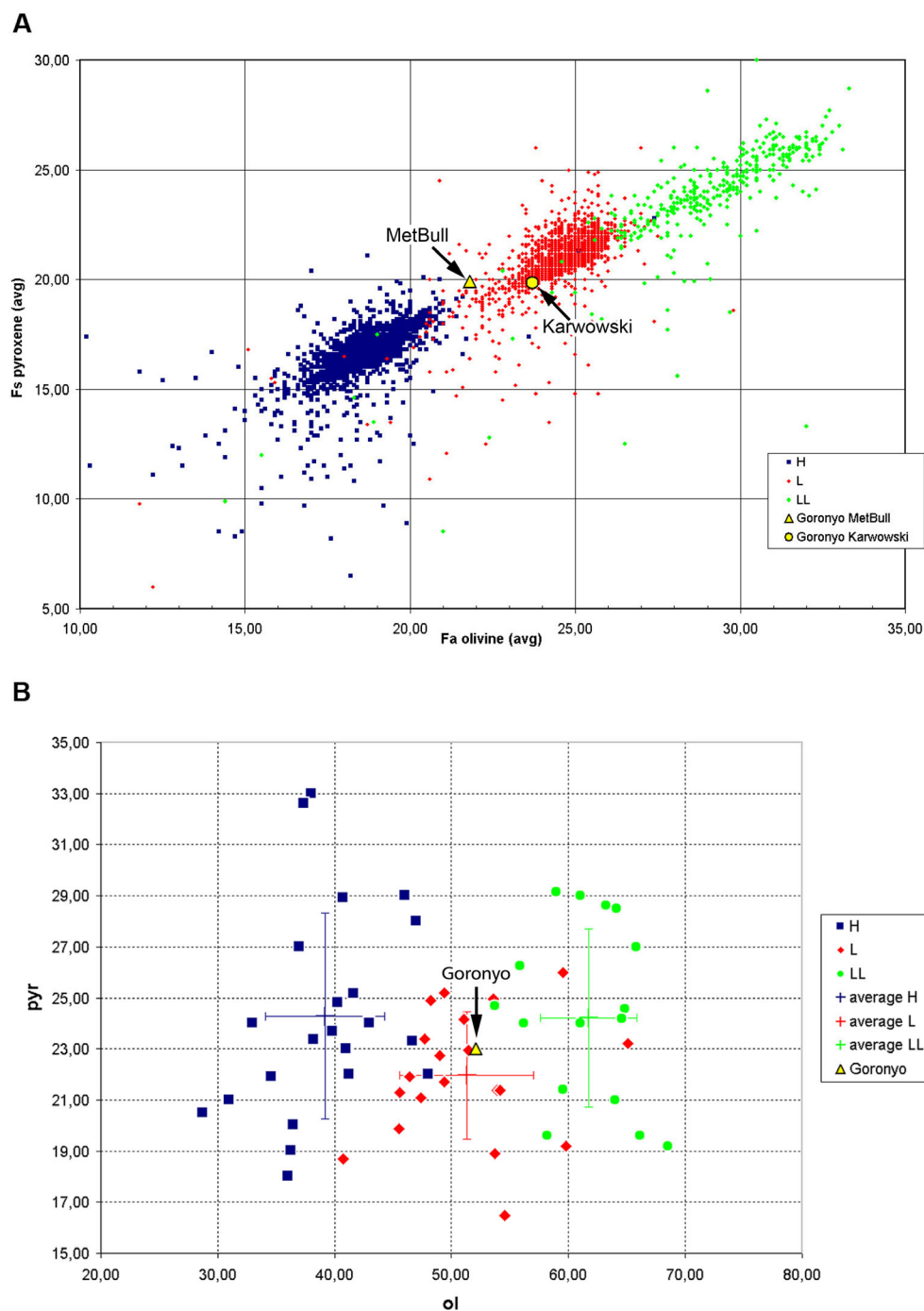


Fig. 3. A) Plot of the amount of the ferrosilite (Fs) in orthopyroxenes versus the amount of the fayalite (Fa) in olivines in ordinary chondrites obtained for 4712 ordinary chondrites (the values taken from Koblitz 2012). B) Plot of the values of Mössbauer spectral data (areas of pyr versus ol) with the position corresponding to meteorite Goronyo.

For each unknown meteorite, the Mahalanobis distance to the centroids of proper three clusters can be calculated. Identifying the proper cluster was determined on the basis of choosing the smallest Mahalanobis distance between the point representing the unclassified

meteorite and the centroid of points representing the ordinary chondrites of types H, L, and LL.

Application of the Mahalanobis distance to the classification of meteorites permits us also to determine the *level of similarity* (S_{cluster}) of the investigated

Table 2. Mean values (MV) of four parameters (ol, pyr, met, and tr) and their population variances (PV) in three different clusters [%]. n = number of samples.

Type	n	MV (ol)	PV (ol)	MV (pyr)	PV (pyr)	MV (met)	PV (met)	MV (tr)	PV (tr)
H	22	39.2	5.1	24.3	4.0	17.3	7.1	16.5	2.6
L	20	51.3	5.7	22.0	2.5	8.4	3.5	15.7	3.5
LL	17	61.7	4.1	24.2	3.5	1.2	1.7	10.6	3.5

Table 3. Values of the correlation matrix for all three clusters (in bold are values of correlation for pairs olivine versus metallic phase—see Fig. 2A).

	ol	pyr	met	tr
Type H				
ol	1			
pyr	0.3028	1		
met	-0.7842	-0.6711	1	
tr	0.2058	0.096	-0.4964	1
Type L				
ol	1			
pyr	0.1373	1		
met	-0.5904	-0.5432	1	
tr	-0.7272	-0.3028	0.144	1
Type LL				
ol	1			
pyr	-0.2128	1		
met	-0.622	-0.0328	1	
tr	-0.4248	-0.6244	0.1336	1

meteorite to the specific cluster. The similarity of the examined meteorite to other objects from clusters types H, L, and LL can be determined.

This similarity (S_{cluster}) should depend not only on the Mahalanobis distance to centroids of the clusters, but also on the particular shapes of the clusters. The set of our variables has a rather complex form. The clusters with more exotic shape (highly elongated, asymmetric, or even ameboidal shape) have the higher tendency to capture the adjacent points stronger.

To define properly our *level of similarity* S_{cluster} , we were working in 1-D space. If we assume that the set of our variables is not very far from a Gaussian distribution, then the *level of similarity* of the unknown meteorite to one of three clusters can be defined on the basis of the probability function $P(y \leq d_M; s_{\text{aver.}})$, when the variable y is smaller or equal to d_M which is described by the formula:

$$P(y \leq d_M; s_{\text{aver.}}) = \int_0^{d_M} \frac{1}{s_{\text{aver.}} \sqrt{2\pi}} e^{\frac{-y^2}{2s_{\text{aver.}}^2}} dy,$$

thus:

Table 4. Unbiased estimators of the covariance matrix (S) for individual clusters in our model and the values of the determinants of the parameters' space (here n = 4).

	ol	pyr	met	tr
Type H				
ol	24.788			
pyr	5.941	15.532		
met	-27.046	-18.320	47.980	
tr	2.642	0.975	-8.868	6.652
det(S) = 7643.096				
Type L				
ol	30.936			
pyr	1.860	5.931		
met	-11.307	-4.555	11.856	
tr	-13.908	-2.535	1.705	11.822
det(S) = 1,036,702				
Type LL				
ol	16.094			
pyr	-2.882	11.397		
met	-4.004	-0.178	2.575	
tr	-5.865	-7.255	0.738	11.845
det(S) = 542,193				

$$S_{\text{cluster}}(\text{the level of similarity to the cluster } [\%]) = (1 - 2 \cdot P(y \leq d_M; s_{\text{aver.}})) \cdot 100\%,$$

where d_M is the Mahalanobis distance of the investigated points to the specific cluster and $s_{\text{aver.}}$ is the “average variance” of the multidimensional cluster.

The definition and the way of determining the “average variance” $s_{\text{aver.}}$ is described in Appendix B.

Taking into account only the Mössbauer spectral areas, we obtained for the Goronyo meteorite (ol = 52.1, pyr = 23.0, met = 6.1, and tr = 16.5; Fig. 3B), the Mahalanobis distance and *level of similarity* S_{cluster} to the three clusters as

	Type H	Type L	Type LL
The Mahalanobis distance d_M (4D)	3.07	0.77	3.54
The <i>level of similarity</i> S_{cluster}	31.6%	74.7%	10.6%

According to the Meteoritical Bulletin Database (2006), meteorite Goronyo is of type H, but according to our results it is most probably of type L.

DISCUSSION

Figure 1 presents Mössbauer spectra of ordinary chondrites type H (Carancas), type L (New Concord), type LL (NWA7733), and Goronyo. At first glance, it is obvious that Mössbauer spectra of ordinary chondrites of different types differ from each other. From type H, to L, to LL the subspectrum of the metallic phase is less and less intense. In the LL type meteorite, it is almost invisible. One can also notice an increasing contribution of the subspectrum related to olivine. This is clearly seen in Fig. 2A. The spectrum of the Goronyo meteorite looks more similar to New Concord (type L) than to Carancas (type H); however, it was classified in the Meteoritical Bulletin as ordinary chondrite type H. We therefore performed independent studies of the Fa and Fs content in a sample of the Goronyo meteorite. The results obtained ($Fa = 23.51 \pm 0.16$ and $Fs = 19.91 \pm 0.06$) suggest that this meteorite is type L.

The next step for elucidation of this problem was using the 4M method for determining which type of ordinary chondrites fits best the Goronyo meteorite. The similarity was the highest for type L (75%), while the similarity to type H was only 32% and to type LL 11%.

How can we explain this discrepancy between our own results and results published in the Meteoritical Bulletin?

Figure 3A presents the dependence of Fs versus Fa for ordinary chondrites types H, L, and LL for 4712 meteorites (data taken from Koblitz 2012). The areas corresponding to meteorites H, L, and LL are well separated from each other. The point representing the Goronyo meteorite taken from the data of the MetBull is shown by the yellow triangle and is located on the border between the H and L areas, but the point obtained from our own measurements is shown by the yellow circle and lies inside the L area. The value of Fs is the same, yet the Fa value is different (21.8 versus 23.51 ± 0.16). The classical method for the classification of ordinary chondrites, based on microprobe results (Fredriksson and Keil 1964), implies several restrictive conditions regarding investigated meteorites. However, one cannot exclude an impact of inhomogeneity of the meteorites on the results obtained by the microprobe method.

Figure 3B shows the relation between the iron content in pyroxenes and the iron content in olivine in the 59 meteorites from our database. On this plot, the point representing our sample of the Goronyo meteorite (yellow triangle) is located in the center of the area of ordinary chondrites type L. This result points to the

effectiveness of this method for classification of ordinary chondrites by Mössbauer spectroscopy.

CONCLUSIONS

It appears that the 4M method could become a complementary method for classification of ordinary chondrites. Its main advantage is related to the use of data from all four principal mineral phases present in ordinary chondrites. These data can be obtained during one Mössbauer measurement of the meteoritic sample weighting about 100 mg.

It is important to note that ordinary chondrites are highly nonhomogeneous and the concentrations of the main mineralogical phases vary in wide ranges between H, L, and LL types. These ranges are much larger than the uncertainties in the determination of percentages of spectral areas obtained by Mössbauer measurements. As an example, the range of the percentages of metallic phases in ordinary chondrites type H is from 10 to 30%, while the experimental error in measurements of the spectral areas by Mössbauer spectroscopy is less than 3%. As experimental errors are much smaller than the natural spread of the values of the percentages of spectral areas, it is obvious that increasing the number of measured meteoritic samples is more important than the attempts to decrease experimental errors in Mössbauer spectroscopy areas evaluations.

The increase in the number of meteorites measured which constitute the basis for the 4M method may be a useful way to the impact of inhomogeneity of meteoritic material in classifying meteorites.

Acknowledgments—We thank Prof. Erika R. Bauminger for fruitful discussion. We thank Marcin Cimała, Ansgar Greshake, Mike Gilmer, Tomasz Jakubowski, Kazimierz Mazurek, Jarosław Morys, Krzysztof Socha, Robert Verish, Łukasz Karwowski, and Jan Woreczko for generously supplying the samples of meteorites for this study.

Editorial Handling—Dr. A. J. Timothy Jull

REFERENCES

- Abdu Y. A. and Ericsson T. 1997. Mössbauer spectroscopy, X-ray diffraction, and electron microprobe analysis of the New Halfa meteorite. *Meteoritics & Planetary Science* 32:373–375.
- Baek K. S., Park Y. S., and Ok H. N. 1984. Effects of vanadium impurities on the crystallographic and spin-rotation transitions of iron sulfide. *Physical Review* 30:404–406.
- Bland P. A., Sexton A. S., Jull A. J. T., Bevan A. W. R., Berry F. J., Thornley D. M., Astin T. R., Britt D. T., and Pillinger C. T. 1998. Climate and rock weathering: A study

- of terrestrial age dated ordinary chondritic meteorites from hot desert region. *Geochimica et Cosmochimica Acta* 62:3169–3184.
- Bogusz P., Brzózka K., Górka B., Szumiata T., Woźniak M., and Gałazka-Friedman J. 2018. Classification of meteorites—Mössbauer comparative studies of three ordinary chondrites measured in different laboratories. *Acta Physica Polonica A* 134:1070–1075.
- Connolly H. C. Jr., Zipfel J., Grossman J. N., Folco L., Smith C., Jones R. H., Richter K., Zolensky M., Russell S. S., Benedix G. K., Yamaguchi A., and Cohen B. A. 2006. The Meteoritical Bulletin, No. 90. *Meteoritics & Planetary Science* 41(9):1383–1418.
- Elewa N. N. and Cadogan J. M. 2017. An ^{57}Fe Mössbauer study of the ordinary chondrite meteorite Lynch 001. *Hyperfine Interactions* 238:1–7.
- Fisher R. A. 1936. The use of multiple measurements in taxonomic problems. *Annals of Eugenics* 7:179–188.
- Fredriksson K. and Keil K. 1964. The iron, magnesium and calcium distribution in coexisting olivine and rhombic pyroxenes in chondrites. *Journal of Geophysical Research* 69:3487–3515.
- Gałazka-Friedman J., Szlachta K., Karwowski Ł., and Woźniak M. 2014. Mössbauer studies of Soltmany and Shisr 176 meteorites—Comparison with other ordinary chondrites. *Hyperfine Interactions* 226:593–600.
- Gałazka-Friedman J., Woźniak M., Duda P., Rzepecka P., Jakubowska M., and Karwowski Ł. 2017. Mössbauer spectroscopy—A useful method for classification of meteorites? *Hyperfine Interactions* 238:11.
- Hafner S. S., Evans B. J., and Kalvius G. M. 1967. Second order effect in the hyperfine field of Fe^{57} in troilite (anti-ferromagnetic FS). *Solid State Communications* 5:17–19.
- Koblitz J. 2012. MetBase. Meteorite data retrieval software, Version 7.3 (CD-ROM), Ritterhude, Germany.
- Kruse O. 1990. Mössbauer and X-ray study of the effect of vacancy concentration in synthetic hexagonal pyrrhotites. *American Mineralogist* 75:755–763.
- Krzanowski J. 2000. *Principles of multivariate analysis: A user's perspective*. Oxford: Oxford University Press.
- Lagarec K. and Rancourt D. G. 1998. *Recoil: Mössbauer spectral analysis software for Windows*, version 1.0. Ottawa, Canada: Department of Physics, University of Ottawa.
- Lipka J., Sitek J., Dekan J., Degmová J., and Porubčan V. 2013. Mössbauer study of Slovak meteorites. *Hyperfine Interactions* 218:107–111.
- Mahalanobis P. C. 1936. On the generalized distance in statistics. *Proceedings of the National Institute of Sciences of India* 2:49–55.
- Maksimova A. A., Oshtrakh M. I., Chukin A. V., Felner I., Yakovlev G. A., and Semionkin V. A. 2018. Characterization of Northwest Africa 6286 and 7857 ordinary chondrites using X-ray diffraction, magnetization measurements and Mössbauer spectroscopy. *Spectrochimica Acta Part A* 192:275–284.
- Mason B. H. 1962. *Meteorites*. New York: John Wiley & Sons Inc.
- Meteoritical Bulletin Database* (2006), <https://www.lpi.usra.edu/meteor/>. Accessed May 2019.
- Morrison D. F. 1990. *Multivariate statistical Methods*. New York, NY: McGraw-Hill.
- Ok H. N., Baek K. S., and Kim C. S. 1982. Mössbauer study of $\text{Cr}_x\text{Fe}_{1-x}\text{S}$. *Physical Review B* 26:5223–5225.
- Ortalli I. and Pedrazzi G. 1990. Study of the Torino meteorite. *Hyperfine Interactions* 57:2275–2278.
- Oshtrakh M. I., Petrova E. V., Grokhovsky V. I., and Semionkin V. A. 2008. A study of ordinary chondrites by Mössbauer spectroscopy with high velocity resolution. *Meteoritics & Planetary Science* 43:941–958.
- Paliwal B. S., Tripathi R. P., Verma H. C., and Sharma S. K. 2000. Classification of the Didwana-Rajod meteorite: A Mössbauer spectroscopic study. *Meteoritics & Planetary Science* 35:639–642.
- Szlachta K., Gałazka-Friedman J., and Woźniak M. 2014. Porównawcze badania mössbauerowskie meteorytów: Soltmany (L6), Chelyabinsk (LL5) i Grzempy (H5) (Mössbauer comparative studies of the Soltmany (L6), Chelyabinsk (LL5) and Grzempach (H5) meteorites). *Acta Societatis Metheoriticae Polonorum* 5:115–120.
- Verma H. C., Rawat A., Paliwal B. S., and Tripathi R. P. 2002. Mössbauer spectroscopic studies of an oxidized ordinary chondrite fallen at Itawa-Bhopji, India. *Hyperfine Interactions* 142:643–652.
- Verma H. C., Jee K., and Tripathi R. P. 2003. Systematics of Mössbauer absorption areas in ordinary chondrites and applications to a newly fallen meteorite in Jodhpur, India. *Meteoritics & Planetary Science* 38:963–967.
- Zhang Y., Stevens J. G., Li Y., and Li Z. 1994. Mössbauer study of the Jilin and Xingyang meteorites. *Hyperfine Interactions* 91:547–550.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

Table S1. Percentages of spectral areas associated with olivine (ol), pyroxene (pyr), metallic phase (met), troilite (tr) for ordinary chondrites type H, L and LL.

APPENDIX A

There are many ways to calculate a distance in mathematics. Beside the best known Euclidean distance, there are other methods such as Manhattan distance, Chebyshev distance, Hausdorff distance, and the Mahalanobis distance. Mahalanobis distance is usually

applied to statistics problems (e.g., Cluster Analysis) whenever we want to find the similarity between an unknown random vector and a vector representing a known cluster.

Figure A1 explains the idea of Mahalanobis distance (d_M) for a 2-D case in simple words. The Mahalanobis distances from points 1 and 2 to the “center of the cluster” are equal to each other, but are smaller than the Mahalanobis distance from point 3 to the center of cluster.

$$d_{M1} = d_{M2} < d_{M3}.$$

Measuring the Euclidean distance from points 1, 2, and 3 to the “center of the cluster,” we will find the following inequality:

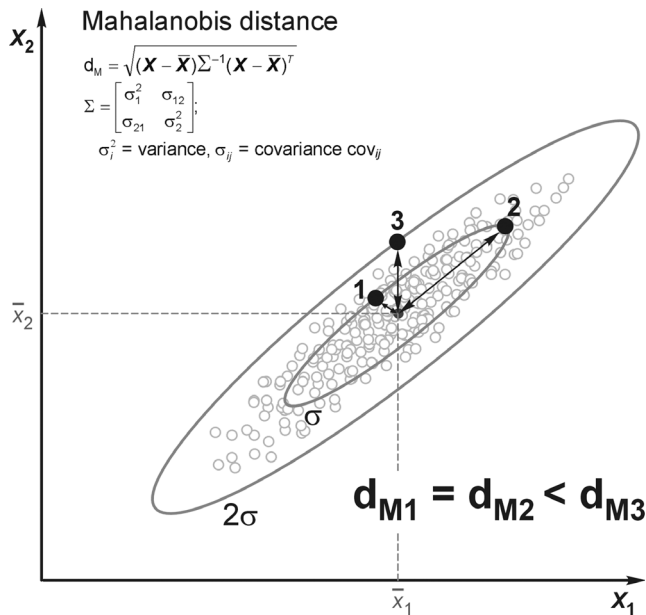


Fig. A1. Example of the Mahalanobis distance (d_M) for 2-dimensional case.

$$d_1 < d_3 < d_2.$$

The Mahalanobis distance (Mahalanobis 1936) between tested point X (n -dimensional vector) and the cluster described by average values \bar{X} and covariance matrix Σ is defined by the formula:

$$d_M = \sqrt{(X - \bar{X})\Sigma^{-1}(X - \bar{X})^T},$$

where, \bar{X} is the vector of the average values for all variables (so called centroid) and Σ is the covariance matrix of the cluster.

The example of the difference between the Euclidean distance and Mahalanobis distance for 2-dimensional case is shown in Fig. A2.

APPENDIX B

How to define our “average variance” $\sigma_{\text{aver.}}$ of multidimensional cluster described by the covariance matrix Σ ?

Our 4-D cluster is described by covariance matrix (Σ), but it is not a diagonal matrix (because of the existing correlations between parameters). So the shape of the 4-D ellipsoid is not known. It means that the values of the variances on the diagonal of the covariance matrix Σ are not the values which we are looking for. We are looking for variances in such a system of linear

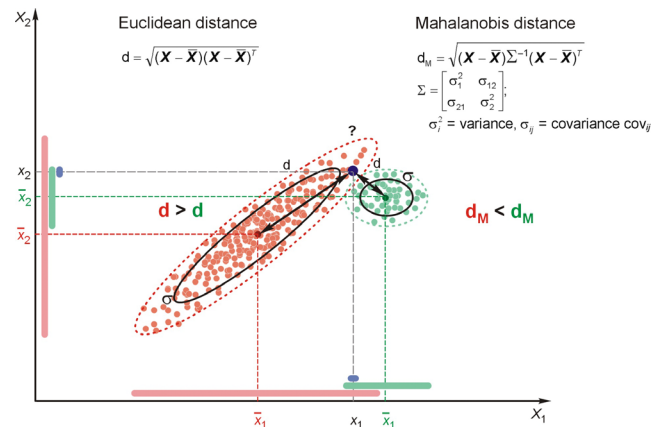


Fig. A2. Example of the difference between the Euclidean distance (d) and Mahalanobis distance (d_M) in 2-D space for two clusters. To illustrate how the shape of the clusters influences the values of different types of distances, clusters with very different shapes were chosen. One of the clusters is very elongated and the other is round. The Euclidean distance to the centroid of the elongated cluster is higher than to round cluster. On the contrary, the Mahalanobis distance to the centroid of elongated cluster is smaller than to the round one.

combinations of variables, in which the variances are not correlated (see Fig. B1).

For determination of the “average variance” $\sigma_{\text{aver.}}$, we decided to use properties of the covariance matrix and principal component analysis (PCA). The covariance matrix is symmetric—so it could be diagonalized ($\Lambda = A^T \Sigma A$, where A is the orthogonal matrix and Λ is the diagonal matrix) (Morrison 1990; Krzanowski 2000). The values on diagonal of the matrix Λ are appropriate to the principal component and are equal to eigenvalues (λ_i) of the covariance matrix Σ . So, we can use the properties of the determinant of the matrix Λ :

$$\det(\Lambda) = \lambda_1 \cdot \lambda_2 \cdot \lambda_3 \cdot \lambda_4 = \det(\Sigma),$$

where λ_i is the eigenvalues of the diagonalized matrix Σ , which are equal to the variances along of the principal components (Krzanowski 2000) (see Fig. B1).

For calculation of the *level of similarity* S_{cluster} , we decided to use the average variance of the n -dimensional cluster. We suggested to define it in a specific way. The clusters with nontypical shape should have “average variance” $\sigma_{\text{aver.}}$ smaller than “regular clusters” (e.g., clusters in the form of the n -dimensional sphere). Let us imagine two 3-D clusters. One has shape similar to the disk with variances along the principal axes equal, for example, $k_1 = 1.00$, $k_2 = 4.00$, $k_3 = 4.00$, and another one quite spherical with $\lambda_1 = \lambda_2 = \lambda_3 = 3.00$. The disk-like cluster should have “smaller” variance. If we define

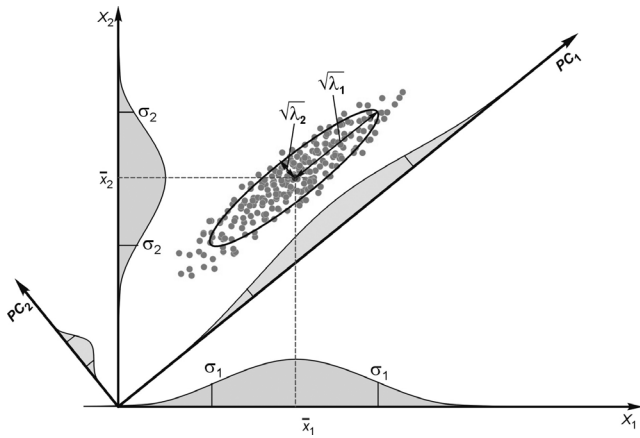


Fig. B1. Example of the cluster with nondiagonal matrix of covariances (correlated variables) in original system of the coordinates (X) and its description in the space of the principal component (PC) analysis, where the variables are not correlated.

“average variance” as arithmetic mean of λ_i , than for two clusters the value will be the same and equal to 3.00. The geometric mean would describe the situation

much better and would be always true for any set of positive numbers $\mathbf{a} = (a_1, \dots, a_n)$, for which the relation: geometric mean $\mathbf{a} \leq$ arithmetic mean \mathbf{a}

is satisfied. The equality occurs when all numbers are equal (for each i and j , $a_i = a_j$). In our case, it happens for the spherical cluster. In case of our two exemplary clusters, we would get: for disk cluster—mean = 2.519 and for spherical cluster—mean = 3.00. Therefore, the geometric mean was chosen for further calculations (it is proportional to the volume of the n -dimensional cluster).

Thus, “the average variance” $\sigma_{\text{aver.}}$ (for n -dimensional space) defined here in this article is equal to the geometric average of the eigenvalues of the covariance matrix Σ :

$$\sigma_{\text{aver.}} = \sqrt[n]{\lambda_1 \cdot \lambda_2 \cdot \lambda_3 \cdot \lambda_4} = \sqrt[n]{\det(\Sigma)}$$

It means that it is $2n$ -th root of the determinant of the covariance matrix $\det(\Sigma)$, where n is dimension of the parameters' space (here $n = 4$).